

PATENT

Docket No. IL-9940B

Assistant Commissioner for Patents  
Washington, DC 20231

## NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of Inventor(s):  
**Mehdi Balooch, Long N. Dinh, Wigbert J. Siekhaus**

For (title): **LOW WORK FUNCTION SURFACE LAYERS PRODUCED BY LASER  
ABLATION USING SHORT-WAVELENGTH PHOTONS**

## 1. Type of Application

- ☐ This new application is for an original patent.
- ☒ This new application is a:
- ☒ Division
  - ☐ Continuation
  - ☐ Continuation-in-part (CIP)

## 2. Benefit of Prior U.S. Application(s) (35 USC 120)

- ☒ The new application being transmitted claims the benefit of prior U.S. application(s). 09/080,109 filed 5/18/98
- ☒ Group/Art Unit: 1762
  - ☒ Examiner of Prior Application: M. Padgett

3. ☐ Benefit under 35 U.S.C. 119(e) of United States provisional application(s) listed below:

Application Serial No.	Filing Date
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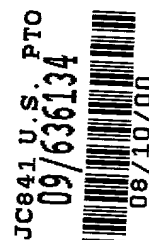
## 4. Papers enclosed which are required for filing Date Under 37 CFR 1.53(b).

17 Pages of specification, including  
Claims, Abstract and Title Page

1 Sheets of drawings

## 5. Additional papers enclosed

- ☒ Preliminary Amendment
- ☒ Express Mail Certificate
- ☒ Return Postcard



09636134-081000

6. **Declaration or oath**

- ☒ Copy from a Prior Application enclosed and executed by
  - ☒ Inventors
  - ☐ legal representative of inventor(s) 37 CFR 1.42 or 1.43
- ☐ Not Enclosed

7. **Assignment**

- ☐ An assignment of the invention to The Regents of the University of California.
  - ☐ is attached
  - ☐ will follow
  - ☒ Previously filed

8. **Certified Copy**

Certified copy(ies) of application(s)

(country)	(application no.)	(filed)
(country)	(application no.)	(filed)

from which priority is claimed

- ☐ is(are) attached.
- ☐ will follow

9. **Fee Calculation**

CLAIMS AS FILED					
Type of Claim	Number Filed	Included in Basic Fee	Number Extra	Rate	Total Fee
Total Claims	12	-20 =	0	x \$18 =	\$ .00
Independent Claims	3	-3 =	0	x \$78 =	\$ .00
				Multiple Claims =	\$
				Basic Filing Fee =	\$ 690.00
				Sub-Total =	\$ 690.00
				Small Entity Filing Fee =	\$ 345.00

1. 1990年12月31日 2. 1991年12月31日 3. 1992年12月31日 4. 1993年12月31日 5. 1994年12月31日 6. 1995年12月31日 7. 1996年12月31日 8. 1997年12月31日 9. 1998年12月31日 10. 1999年12月31日 11. 2000年12月31日 12. 2001年12月31日 13. 2002年12月31日 14. 2003年12月31日 15. 2004年12月31日 16. 2005年12月31日 17. 2006年12月31日 18. 2007年12月31日 19. 2008年12月31日 20. 2009年12月31日 21. 2010年12月31日 22. 2011年12月31日 23. 2012年12月31日 24. 2013年12月31日 25. 2014年12月31日 26. 2015年12月31日 27. 2016年12月31日 28. 2017年12月31日 29. 2018年12月31日 30. 2019年12月31日 31. 2020年12月31日 32. 2021年12月31日 33. 2022年12月31日 34. 2023年12月31日 35. 2024年12月31日 36. 2025年12月31日 37. 2026年12月31日 38. 2027年12月31日 39. 2028年12月31日 40. 2029年12月31日 41. 2030年12月31日 42. 2031年12月31日 43. 2032年12月31日 44. 2033年12月31日 45. 2034年12月31日 46. 2035年12月31日 47. 2036年12月31日 48. 2037年12月31日 49. 2038年12月31日 50. 2039年12月31日 51. 2040年12月31日 52. 2041年12月31日 53. 2042年12月31日 54. 2043年12月31日 55. 2044年12月31日 56. 2045年12月31日 57. 2046年12月31日 58. 2047年12月31日 59. 2048年12月31日 60. 2049年12月31日 61. 2050年12月31日 62. 2051年12月31日 63. 2052年12月31日 64. 2053年12月31日 65. 2054年12月31日 66. 2055年12月31日 67. 2056年12月31日 68. 2057年12月31日 69. 2058年12月31日 70. 2059年12月31日 71. 2060年12月31日 72. 2061年12月31日 73. 2062年12月31日 74. 2063年12月31日 75. 2064年12月31日 76. 2065年12月31日 77. 2066年12月31日 78. 2067年12月31日 79. 2068年12月31日 80. 2069年12月31日 81. 2070年12月31日 82. 2071年12月31日 83. 2072年12月31日 84. 2073年12月31日 85. 2074年12月31日 86. 2075年12月31日 87. 2076年12月31日 88. 2077年12月31日 89. 2078年12月31日 90. 2079年12月31日 91. 2080年12月31日 92. 2081年12月31日 93. 2082年12月31日 94. 2083年12月31日 95. 2084年12月31日 96. 2085年12月31日 97. 2086年12月31日 98. 2087年12月31日 99. 2088年12月31日 100. 2089年12月31日 101. 2090年12月31日 102. 2091年12月31日 103. 2092年12月31日 104. 2093年12月31日 105. 2094年12月31日 106. 2095年12月31日 107. 2096年12月31日 108. 2097年12月31日 109. 2098年12月31日 110. 2099年12月31日 111. 2100年12月31日 112. 2101年12月31日 113. 2102年12月31日 114. 2103年12月31日 115. 2104年12月31日 116. 2105年12月31日 117. 2106年12月31日 118. 2107年12月31日 119. 2108年12月31日 120. 2109年12月31日 121. 2110年12月31日 122. 2111年12月31日 123. 2112年12月31日 124. 2113年12月31日 125. 2114年12月31日 126. 2115年12月31日 127. 2116年12月31日 128. 2117年12月31日 129. 2118年12月31日 130. 2119年12月31日 131. 2120年12月31日 132. 2121年12月31日 133. 2122年12月31日 134. 2123年12月31日 135. 2124年12月31日 136. 2125年12月31日 137. 2126年12月31日 138. 2127年12月31日 139. 2128年12月31日 140. 2129年12月31日 141. 2130年12月31日 142. 2131年12月31日 143. 2132年12月31日 144. 2133年12月31日 145. 2134年12月31日 146. 2135年12月31日 147. 2136年12月31日 148. 2137年12月31日 149. 2138年12月31日 150. 2139年12月31日 151. 2140年12月31日 152. 2141年12月31日 153. 2142年12月31日 154. 2143年12月31日 155. 2144年12月31日 156. 2145年12月31日 157. 2146年12月31日 158. 2147年12月31日 159. 2148年12月31日 160. 2149年12月31日 161. 2150年12月31日 162. 2151年12月31日 163. 2152年12月31日 164. 2153年12月31日 165. 2154年12月31日 166. 2155年12月31日 167. 2156年12月31日 168. 2157年12月31日 169. 2158年12月31日 170. 2159年12月31日 171. 2160年12月31日 172. 2161年12月31日 173. 2162年12月31日 174. 2163年12月31日 175. 2164年12月31日 176. 2165年12月31日 177. 2166年12月31日 178. 2167年12月31日 179. 2168年12月31日 180. 2169年12月31日 181. 2170年12月31日 182. 2171年12月31日 183. 2172年12月31日 184. 2173年12月31日 185. 2174年12月31日 186. 2175年12月31日 187. 2176年12月31日 188. 2177年12月31日 189. 2178年12月31日 190. 2179年12月31日 191. 2180年12月31日 192. 2181年12月31日 193. 2182年12月31日 194. 2183年12月31日 195. 2184年12月31日 196. 2185年12月31日 197. 2186年12月31日 198. 2187年12月31日 199. 2188年12月31日 200.	
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- Page 3 of 3

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant :	Mehdi Balooch et al.	Docket No. :	IL-9940B
Serial No. :		Art Unit :	
Filed :		Examiner :	
For :	Low Work Function Surface Layers Produced By Laser Ablation Using Short-Wavelength Photons		

U.S. PTO  
09/636134  
08/10/00

Commissioner for Patents  
Washington, D.C. 20231

EXPRESS MAIL CERTIFICATE

"Express Mail" label number EL533019771US

Date of Deposit Aug. 10, 2000

I hereby certify that the following *attached* correspondence comprising:

1. New Application Transmittal (original and copy)
2. Preliminary Amendment (2 pages)(original)
3. Verified Statement Claiming Small Entity Status (copy)
4. IL-9940 Application (Specification with Title Page, Claims and Abstract (17 pages), Combined Declaration and Power of Attorney (copy) Drawings (1 sheet) (copy)
5. Power of Attorney By Assignee of Entire Interest (Revocation of Prior Powers)
6. Return Postcard

is being deposited with the United States Postal Service "Express Mail Post Office to addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Box: Patent Application, Commissioner for Patents, Washington, D.C. 20231.

Kathy E. Raymond

(Type or print name of person mailing paper)

Kathy E. Raymond

(Signature of person mailing paper or fee)

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Mehdi Balooch et al.                      Docket No. : IL-9940  
 Serial No. :    Art Unit :  
 Filed :    Batch No. :  
 For : Low Work Function                      Examiner :  
       Surface Layers Produced  
       By Laser Ablation Using  
       Short-Wavelength  
       Photons

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY  
 STATUS [37 CFR 1.9 (f) and 1.27(d)] - NONPROFIT ORGANIZATION**

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

The Regents of the University of California  
 300 Lakeside Drive, 22nd Floor  
 Oakland, CA 94612-3550

**TYPE OF ORGANIZATION**

  X   University or Other Institution of Higher Education

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code with regard to the invention entitled Low Work Function Surface Layers Produced By Laser Ablation Using Short-Wavelength Photons

by inventor(s) Mehdi Balooch/Long N. Dinh/Wigbert J. Siekhaus  
 described in

  X   the specification filed herewith.

       application serial no. \_\_\_\_\_, filed \_\_\_\_\_.

       patent no. \_\_\_\_\_, issued \_\_\_\_\_.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention, except for a license to a Federal Agency pursuant to 35 USC 202(c) (4).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

  X   no such person, concern, or organization

I acknowledge the duty to file, in this application or patent, notification of any charge in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

JANET G. TULK  
Laboratory Counsel  
Lawrence Livermore National Laboratory  
7000 East Avenue, L-701  
Livermore, CA 94551

Janet G. Tulk  
JANET G. TULK

4-26-98  
Date

JC841 U.S. PTO  
09/636134

Applicant :	Mehdi Balooch et al.	Docket No. :	IL-9940
Serial No. :		Art Unit :	
Filed :		Examiner :	
For :	Low Work Function Surface Layers Produced By Laser Ablation Using Short-Wavelength Photons		

Commissioner for Patents  
Washington, D.C. 20231

Kindly amend the above-identified application, which is a division of Application Serial No. 09/080,109 filed May 18, 1998, as follows:

Change the title to read --Apparatus For Depositing A Low Work Function Material --.

Cancel Claims 1-18.

Please add the following claims:

21. The apparatus of Claim 19, additionally including means for maintaining a vacuum in said deposition chamber.

22. The apparatus of Claim 19, additionally including means for heating and cooling said substrate.

23. The apparatus of Claim 19, additionally including an ion gun for surface cleaning the substrate.

24. The apparatus of Claim 19, additionally including a gas generator for producing a flow of molecules on a surface of the substrate.

25. The apparatus of Claim 19, wherein said deposition chamber includes a window through which the short-wavelength photons are directed.

26. The apparatus of Claim 19, wherein said target is composed of barium metal oxide or an alkali metal.

27. The apparatus of Claim 19, wherein said target is retained in a target holder and rotated at 1-10 rpm.

28. The apparatus of Claim 19, wherein said means for holding said substrate is rotated at 1 to 10 rpm and tilted at an angle of 0 to 90°.

29. The apparatus of Claim 19, wherein said laser is selected from the group consisting of NdYAG, an excimer, and wherein said short-wavelength is in the range of 200 to 550 nm.

30. The apparatus of Claim 19, wherein said laser has a pulse length of 6 to 60 nanoseconds, with an energy fluence of 0.2-5 J/pulse.

#### Remarks

Claims 1-18 have been cancelled. New Claims 21-30 have been added. Examination of original Claims 19 and 20 and new Claims 21-30 is requested.

Dated: 8/10/00

Respectfully submitted,



L.E. Carnahan  
Agent for Applicants  
Registration No. 20,555  
Tel. No. (925) 422-5024



SC N 12

S-85,932

RL-13,551

IL-9940



LOW WORK FUNCTION SURFACE LAYERS PRODUCED BY  
LASER ABLATION USING SHORT-WAVELENGTH PHOTONS

BY

Mehdi Balooch (USA)  
551 Colusa Avenue  
Berkeley, CA 94707

Long N. Dinh (USA)  
2011 Olivera Road, #C  
Concord, CA 94520

Wigbert J. Siekhaus (USA)  
1110 Cragmont Avenue  
Berkeley, CA 94708

LOW WORK FUNCTION SURFACE LAYERS PRODUCED BY  
LASER ABLATION USING SHORT-WAVELENGTH PHOTONS

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

BACKGROUND OF THE INVENTION

The present invention relates to forming low work function layers, particularly to producing low work function surface layers on a substrate, and more particularly to a process and apparatus for forming low work function surface layers by laser ablation using short-wavelength photons.

Electron emission from sharp tips due to an applied electric field is an important phenomenon in many technical applications, such as scanning tunneling microscopy and flat panel display technology. In all such applications and, in particular, the two-referenced above, it is important that the tips have low work functions, are smooth on the nanometer scale, and are stable in varying gaseous environments and under high electric field conditions.

It is well known that alkali metal oxides or alkali-metal-silicon oxides on elemental or oxide substrates, show low work functions ( $\sim 1\text{eV}$ ) (see *Handbook of Thermionic Properties* by V. S. Fomenko, G. V. Samsonov ed., Plenum Press Data Division, New York, 1966). Layers of such materials have been applied in the prior art as pastes to be "activated" by various procedures. However, such activation procedures cannot be used for micro-meter-scale protrusions, for example, to be used as field-emitter tips.

It has been found that laser ablation can be performed on targets of arbitrary composition, even on materials of extremely high melting point, such as thorium oxide, and the deposition process is directly in line of sight from the laser impact point so that complicated structures, such as field emitter structures, can be coated at desired locations. Based on these findings, the present invention has been developed which involves a process and apparatus for producing low work function surface layers on substrates by laser ablation using short-wavelength (at or below visible wavelength) photons from low work function targets. The elemental composition of the deposited layer is controlled by the composition of the target and the gaseous environment in which the ablation process is performed.

### SUMMARY OF THE INVENTION

It is an object of the present invention to provide surface layers of low work function material.

A further object is to provide a method and apparatus for depositing low work function material on a substrate.

A further object of the invention is to provide low work function surface layers by laser ablation.

Another object of the invention is to provide a process and apparatus for producing low work function surface layers by laser ablation using short-wavelength photons.

5 Another object of the invention is to provide a process and apparatus for depositing low work function material wherein the elemental composition of the deposit is controlled.

Another object of the invention is to provide a process for depositing low work function material on a substrate and controlling the composition of the deposited material by the composition of a laser ablated target and the gaseous environment in which the ablation is performed.

10 Another object of the invention is to provide sharp tips utilized in electron emission devices with a material having low work functions; and is stable in varying gaseous environments and under high electrical field conditions.

15 Other objects and advantages of the present invention will become apparent from the following description and accompanying drawings. The invention involves depositing low work function surface layers by laser ablation using short-wavelength photons. The short-wavelength photons are at or below visible wavelength. The elemental composition of the deposited low work function material is controlled by the composition of the laser  
20 ablated target, the temperature of the substrate, and the gaseous environment in which the ablation process is performed. The target material is mounted at an angle on a rotatable holder and the substrate on which the deposit is to be made is mounted on a holder that can be rotated, tilted, heated, and cooled.  
25 The apparatus may also include an ion gun for surface cleaning of the substrate, a gas generator for producing a flow of molecules directed at the

substrate, and a supply of gas to control the environment which may be made reactive or changed into radicals on the way to the substrate's surface. Since the substrate can be both rotated and tilted, the ablated material from the target may contact the substrate at various angles, thus enabling, for example, the coating of a sharp tip of a field emission device with a desired low work function material. For example, a barium/SiO<sub>2</sub> glass was ablated onto a substrate using ns-long laser pulses of short-wavelength photons, and the work function of the deposited layer was found to be close to the work function of the barium metal oxide target. For example, the laser ablation may be carried out using an excimer laser or a frequency tripled NdYAG laser. The invention thus has many applications, such as coating electron-emitting surfaces (e.g., filaments, field emitters) for electron microscopes or flat panel displays; or for scanning more microscope tips to reduce work function.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated into and form a part of the disclosure, illustrate an embodiment of the invention and, together with the description, serve to explain the principles of the invention.

Figure 1 schematically illustrates an embodiment of an apparatus for carrying out the process of depositing low work function surface layers by laser ablation in accordance with the present invention.

Figure 2 schematically illustrates a portion of the apparatus of Figure 1 for depositing a surface layer of low work function material on the tip of a field emitter structure.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to depositing low work function material on a surface by laser ablation using short-wavelength photons. The short-wavelength photons are at or below visible wavelength and thus are in the range of 200 to 550 nm. The elemental composition of the deposited low work function layer can be controlled by the composition of the laser ablated target and the gaseous environment in which the ablation process is performed. The invention is particularly applicable for use in fabricating devices using electron emission from sharp tips, such as in tunneling microscopy and flat panel display technology, wherein it is important that the tips: (1) have low work functions, (2) are smooth on a nanometer scale, and (3) are stable in varying gaseous environments and under high electric field conditions. Tests have established that each of these three (3) properties has been achieved by the process and apparatus of the present invention. Since laser ablation can be performed on targets of arbitrary composition, even on materials of extremely high melting point such as thorium oxide, and since here the target is rotated and the substrate to be deposited on can be rotated, tilted, heated, and cooled; and since the deposition process is directional in line of sight from the laser impact point, the low work function material can be deposited on essentially any shaped substrate of various materials. The lasers utilized for producing the desired short-wavelength photons include excimer lasers and frequency tripled NdYAG lasers. For example, an Xe excimer laser producing pulses in the 10 to 30 ns length, and which operates at a wavelength of 308 nm with an energy fluence of 0.5 J/pulse, has been utilized to ablate a barium metal oxide target to deposit a layer of barium/SiO<sub>2</sub> glass onto a substrate, and tests established that the work

function of the deposited layer was close to the work function of the barium metal oxide target.

The objective of the present invention is to create at the surface of a substrate a layer having a work function different from that of the substrate by laser-ablating a material of the desired composition onto the substrate of interest. The composition of the deposit is to be controlled by the ablation-target's composition, target's temperature, and by the composition of the environment in which the ablation process occurs. Thus, using the same target composition and changing the composition of the environment, different compositions of the deposited material may be provided.

In the particular implementation of the invention to experimentally verify the deposition process, the substrate to be surface-modified was introduced into a deposition chamber that could be evacuated to ultra high vacuum (UHV) conditions or filled with suitable gases from an exterior supply line. The target material was mounted onto a holder that spins the target during laser deposition so that subsequent pulses hit different target spots. The substrate is mounted onto a device that can heat or cool it over a wide range of temperatures, spin the substrate during a series of deposition pulses, and tilt/spin the substrate during deposition. Alternative other means (such as a laser) can be employed to change the substrate's surface temperature by delivering energy to it from the outside of the chamber. The substrate can be made to face, simultaneously or separately, a variety of devices for cleaning or processing the substrate surface, such as a Knudsen cell capable of generating a flow of molecules directed at the surface or an ion gun. Naturally occurring surface contaminations, such as the surface oxide, were removed by heating the substrate such that the

contamination volatilizes or is "burned" by the introduction of a suitable reactive gas from the outside, or/and by simultaneous ion bombardment with suitable noble gas ions. Gases introduced from the outside may be made more reactive by dissociating them or changing them into radicals on their way to the substrate's surface. Surface cleanliness may be monitored in situ by instrumentation, such as an Auger Analyzer. The simultaneous use of all or some of these tools makes it possible to controllably create surface layers containing elements introduced from interior and exterior gas sources and the ablation target. Thus a wide range of surface-layer-compositions can be produced. For example, as pointed out above, a barium/SiO<sub>2</sub> glass was ablated onto a substrate and the work function of the surface layer thus deposited was measured by photoelectron spectroscopy and Kelvin Probe, and it was found to be close to the work function of the barium metal oxide target which was ablated onto the substrate.

Figure 1 illustrates an embodiment of an apparatus which includes components that can be utilized to produce or deposit a variety of compositions of low work function material from the same target on a substrate. As shown, the Figure 1 apparatus comprises a deposition chamber 10 having a window 11 therein through which an externally located short-wavelength laser 12 directs pulses of energy indicated at 13 onto a target 14 retained by an ablation target holder 15 located in deposition chamber 10, and which may be rotated as known in the art by drive means indicated at 15'. Located externally of and operatively connected to deposition chamber 10 is a vacuum pump 16 capable of evacuation of chamber 10 to ultra high vacuum (UHV) conditions, if desired. Also located externally is an exterior supply of gas 17 to which is connected a gas doser 18 (with atomizer and radical



generator) located within deposition chamber 10 and constructed, as indicated at 19, to direct gas onto a substrate 20 on which low work function material is to be deposited. The substrate 20 is mounted to a substrate holder 21, which is connected to a driver 22 located externally of deposition chamber 10, whereby the holder 21 can be rotated, tilted, or tilted and rotated. The substrate holder 21 is also connected to means indicated generally at 23 and located externally for heating or cooling the substrate 20. Drive mechanisms for rotating a target and for rotating/tilting a substrate holder and means for heating/cooling a substrate are known in the deposition art and thus need not be herein described in detail. Located within deposition chamber 10 are an ion gun 24 for surface cleaning the substrate 20, as indicated by arrow 25, and a gas generator 26 for producing a flow of molecules on the surface of the substrate 20, as indicated by arrow 27. The ion gun 24 and gas generator 26 may be located externally of chamber 10, with openings provided in the chamber to enable treatment of the substrate thereby.

As shown in Figure 1 and after the surface of substrate 20 has been cleaned, the composition of the environment within deposition chamber 10 has been determined and established, and with the ablation target holder 15 and substrate holder 21 rotating, pulses of laser energy 13 from short-wavelength laser 12 are directed through window 11 onto rotating target 14, whereby material is ablated from the target 14 onto the surface of substrate 20 as indicated by arrows 28, whereby a layer of low work function material from target 14 is deposited on substrate 20.

By way of example, the substrate 20 may be composed of glass, plastics, ceramics, semiconductor materials such as Si and GaAs, or metal; the target 14 may be composed of barium metal oxide or an alkali metal oxide; the

exterior gas supply 17 may contain oxygen, ozone, or water vapor. The gas generator 26 may be constructed to produce molecules of oxygen, atomic oxygen, hydrogen, or alkali metal vapor. The target holder 15 may be rotated at 1 to 10 rpm, and the substrate holder 21 may be rotated at 1 to 10 rpm and tilted at an angle of 0 to 90°. The substrate holder 21 may be constructed to enable heating of the substrate 20 to up to 500° C, or cooled to liquid nitrogen temperature (77°C). The short-wavelength laser may be an NdYAG laser or an excimer laser, with the short-wavelength being in the range of 200 to 550 nm, with the laser pulse being of a length of 6 to 60 nanoseconds, with an energy fluence of 0.2-5 J/pulse.

As a specific example, a target of barium oxide doped in SiO<sub>2</sub> (dopant level: 10→20%) was ablated by an Xe type excimer laser producing 30 ns pulses of 308 nm wavelength photons onto a silicon substrate, the substrate preparation (cleaning) and the environment conditions within the deposition chamber were as follows:

The Si substrate was first sputtered clean by an Ar ion current of 100 nA at 5 kV for 15 minutes, then flash-heated to 1000°C. The deposition chamber was initially pumped to 10<sup>-8</sup> Torr before oxygen was leaked into the system up to 10<sup>-2</sup> Torr. At this moment, the excimer laser beam was focused to a spot of about 0.5 mm in diameter on the barium silicon oxide target. Operating the laser with a fluence of 0.5 J/pulse at 1 Hz for 20 seconds yielded a deposition layer of about 2.5 nm on the Si substrate. The substrate to target distance was about 25 cm.

In another example of the process of the invention, a 2 nm barium-silicon-oxide layer was deposited on a Mo substrate cleaned and ablated as follows:

The Mo substrate was first sputtered clean by an Ar ion current of 100 nA at 5 kV for 15 minutes, then flash-heated to 1200°C. The deposition chamber was initially pumped to  $10^{-10}$  Torr before oxygen was leaked into the system up to  $10^{-3}$  Torr. Operating the laser in the 4th harmonic (266 nm) with a fluence of 0.35 J/pulse at 10 Hz for 2 seconds yielded a deposition layer of about 2 nm barium oxide on the Mo substrate. The substrate to target distance was about 30 cm.

As pointed out above, the apparatus and process of the invention has application for the fabrication and/or coating of electron-emitting surfaces, or modifying surfaces such that they do easily emit electrons, or coating scanning probe microscope tips to reduce work-function. Figure 2 illustrates an example of the process for coating an electron-emitting surface utilizing the apparatus of Figure 1. As shown in Figure 2, a substrate (electron-emitting surface) 30 is mounted on a substrate holder 21' driven (rotated and/or tilted) by a driver mechanism 22', and a mask or barrier plate 31 having an opening 32 is positioned adjacent the tip 33 of substrate 30, whereby the tip 33 is coated at 34 with a low work function material laser ablated from a target, as indicated by arrow 36. Due to the angle or orientation of the laser plume indicated by 37, the arrow 36, the substrate 30 is tilted and rotated such that the ablated material passes thorough opening 32 in barrier or mask 31 onto tip 33 of substrate 30, whereby only the tip 33 is coated by the ablated material 36, the area of barrier 31 around opening 32, indicated at 38, prevents the body of substrate 30 from being coated.

It has thus been shown that the present invention produces low work function surface layers by laser ablation using short-wavelength photons. The composition of the surface layers of low work function

material can be controlled by the composition of the laser ablated target and the gaseous environment in which the ablation process occurs. Electron-emitting surfaces (filaments, field emitters, etc.) having sharp tips, for example, can be produced wherein the tips have low work functions, and are stable in varying gaseous environments and under high electric field conditions. Thus electron-emitting devices coated by the process of the present invention find applications in scanning tunneling microscope and flat panel display technology, for example.

While a particular apparatus and particular process operations, along with materials, parameters, etc., have been described or illustrated to exemplify and teach the principals of the invention, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.

THE INVENTION CLAIMED IS

1. In a process for depositing low work function material on a substrate, the improvement comprising:  
ablating onto the substrate material from a target of low work function material by laser ablation using short-wavelength photons.
2. The improvement of Claim 1, additionally including rotating the target.
3. The improvement of Claim 1, additionally providing a holder for the substrate, which has characteristics selected from the group consisting of rotatable, tiltable, heatable, and coolable.
4. The improvement of Claim 1, additionally including controlling the elemental composition of the deposited low work function material by controlling the gaseous environment in which the ablation is performed.
5. The improvement of Claim 4, wherein the elemental composition of the deposited low work function material is controlled by controlling the composition of the target.

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8. The improvement of Claim 1, additionally including cleaning the surface of the substrate prior to depositing the low work function material thereon.

10. The improvement of Claim 1, additionally including removing surface contaminations on the substrate prior to depositing the low work function material thereon.

11. The improvement of Claim 10, wherein removing surface contaminations is carried out by at least one of the group consisting of heating the substrate such that the contamination volatilizes, burning the contamination by the introduction of a suitable reactive gas, by ion bombardment with suitable noble gas ions.

12. The improvement of Claim 1, additionally including heating the surface of the substrate by laser energy.

13. The improvement of Claim 1, additionally including controlling the gaseous environment during ablation of the target.

14. The improvement of Claim 13, wherein controlling the gaseous environment is carried out by introducing gases into the environment and directing the gases onto the surface of the substrate making the gases more reactive by dissociating the gases or changing the gases into radicals on their way to the substrate's surface.

15. A process for depositing low work function surface layers, comprising:  
providing a deposition chamber  
providing in the chamber a target containing a low work function material,  
positioning in the chamber a substrate on which low work function material is to be deposited,  
controlling the environment of the deposition chamber, and  
laser ablating the target using photons at or below visible wavelength.

whereby a surface layer of low work function material is deposited on the substrate.

16. The process of Claim 15, additionally including rotating the target.

17. The process of Claim 15, additionally providing means whereby the substrate can be rotated, tilted, heated, or cooled.

18. The process of Claim 15, additionally providing means for processing the surface of the substrate prior to depositing the low work function material thereon.

19. An apparatus for depositing a low work function material on a substrate by laser ablation using short-wavelength photons, including:

5 a deposition chamber,  
a target containing low work function material in said chamber,  
a laser capable of directing short-wavelength photons into said  
chamber and onto said target,  
means for rotating said target,  
means for controlling the environment of said deposition chamber,  
a substrate located in said chamber,  
10 means for holding said substrate, and  
means for at least rotating said substrate.

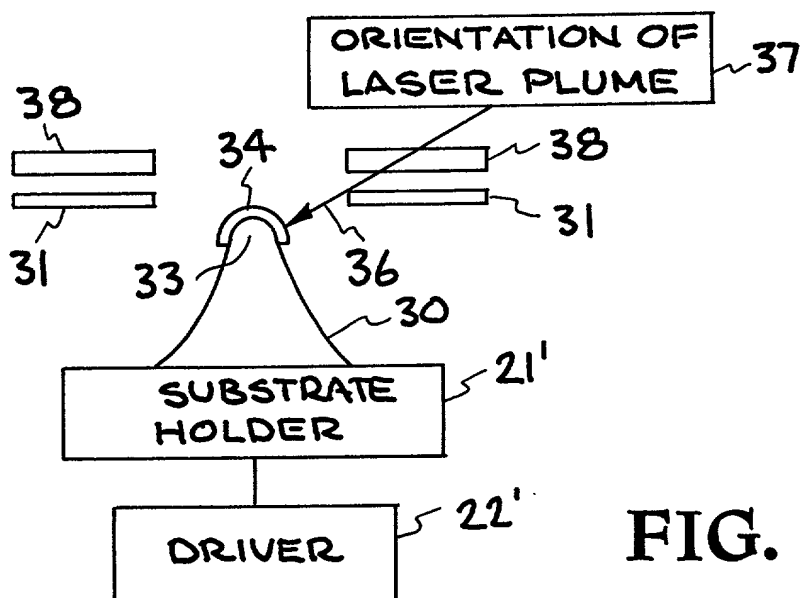
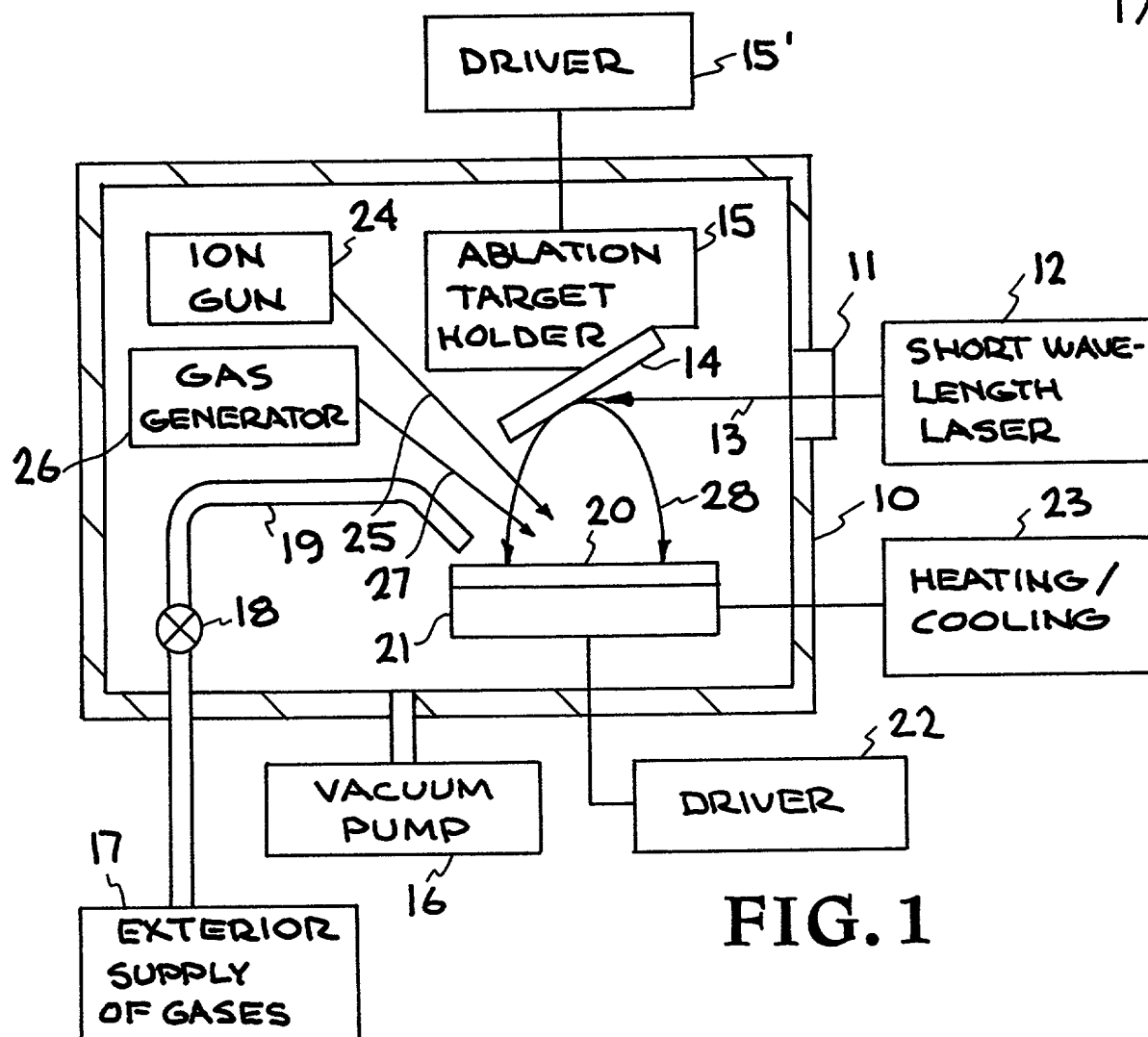
20. The apparatus of Claim 19, additionally including means for heating, cooling, and tilting said substrate, and means for processing the surface of the substrate.



ABSTRACT OF THE DISCLOSURE

Short-wavelength photons are used to ablate material from a low work function target onto a suitable substrate. The short-wavelength photons are at or below visible wavelength. The elemental composition of the deposit is controlled by the composition of the target and the gaseous environment in which the ablation process is performed. The process is carried out in a deposition chamber to which a short-wavelength laser is mounted and which includes a substrate holder which can be rotated, tilted, heated, or cooled. The target material is mounted onto a holder that spins the target during laser ablation. In addition, the deposition chamber is provided with a vacuum pump, an external gas supply with atomizer and radical generator, a gas generator for producing a flow of molecules on the substrate, and a substrate cleaning device, such as an ion gun. The substrate can be rotated and tilted, for example, whereby only the tip of an emitter can be coated with a low work function material.

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## COMBINED DECLARATION AND POWER OF ATTORNEY

As the below named inventor(s), I (we) hereby declare that:

My (Our) residence, post office address and citizenship(s) are as stated below next to my (our) name(s).

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: LOW WORK FUNCTION SURFACE LAYERS PRODUCED BY LASER ABLATION USING SHORT-WAVELENGTH PHOTONS

the specification of which (check one)

X is attached hereto \_\_\_\_\_ was filed on \_\_\_\_\_ as Serial No. \_\_\_\_\_

and was amended on \_\_\_\_\_ (if applicable).

I (We) hereby state that I (we) have reviewed and understand the contents of the above-identified specification, including claims, as amended by any amendment referred to above.

I (We) acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I (We) hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Serial No.	Filing Date	Status
NONE		

<b>POWER OF ATTORNEY:</b> As the named inventor(s), I (we) hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark office connected therewith.	
Names and Registration Nos.	
Henry P. Sartorio L.E. Carnahan	28,535 20,555
<u>Send Correspondence To:</u> Daryl S. Grzybicki Office of Laboratory Counsel for Patents Lawrence Livermore National Laboratory P.O. Box 808 - L-703 Livermore, California 94551	<u>Direct Telephone Calls To:</u> (Name and Telephone Numbers)  Daryl S. Grzybicki (925) 422-7274

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

MEHDI BALOOCH	<i>Mehdi Balooch</i>
Full Name of Inventor	Signature
BERKELEY, CALIFORNIA	4-30-98
Residence (City, State or Foreign Country)	Date
551 COLUSA AVENUE, BERKELEY, CA 94707	USA
Postal Address (Street, City, State, Zip Code)	Citizenship
XX	
LONG N. DINH	<i>Long N. Dinh</i>
Full Name of Inventor	Signature
CONCORD, CALIFORNIA	04-30-98
Residence (City, State or Foreign Country)	Date
2011 OLIVERA ROAD, #C, CONCORD, CA 94520	USA
Postal Address (Street, City, State, Zip Code)	Citizenship
XX	
WIGBERT J. SIEKHAUS	<i>Wigbert J. Siekhaus</i>
Full Name of Inventor	Signature
BERKELEY, CALIFORNIA	4-30-98
Residence (City, State or Foreign Country)	Date
1110 CRAGMONT AVENUE, BERKELEY, CA 94708	USA
Postal Address (Street, City, State, Zip Code)	Citizenship
XX	
Full Name of Inventor	Signature
Residence (City, State or Foreign Country)	Date
Postal Address (Street, City, State, Zip Code)	Citizenship
XX	
Full Name of Inventor	Signature
Residence (City, State or Foreign Country)	Date
Postal Address (Street, City, State, Zip Code)	Citizenship

Practitioner's Docket No. IL-9940

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Mehdi Balooch et al.

Docket No. : IL-9940

Serial No. : 09/080,109

Art Unit : 1762

Filed : 5/18/98

Examiner : M. Padgett

For : Low Work Function Surface Layers Produced By Laser Ablation Using Short-Wavelength Photons

☐ Patent No.\*: Issued:  
\*Note: Insert name(s) of inventor(s) and title also for patent.

Commissioner for Patents  
Washington, D.C. 20231

POWER OF ATTORNEY BY ASSIGNEE OF ENTIRE INTEREST  
(REVOCATION OF PRIOR POWERS)

As assignee of record of the entire interest of the above identified:

- ☒ application,  
☐ patent,

REVOCATION OF PRIOR POWERS OF ATTORNEY

all powers of attorney previously given are hereby revoked and

NEW POWER OR ATTORNEY

the following attorney(s) and/or agent(s) are hereby appointed to prosecute and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

Alan H. Thompson 29,981  
L.E. Carnahan 20,555

(check the following item, if applicable)

- ☐ Attached, as part of this power of attorney, is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

(Power of Attorney by Assignee of Entire Interest [12-2]—page 1 of 2)



SEND CORRESPONDENCE TO:

Alan H. Thompson  
Assistant Laboratory Counsel  
Lawrence Livermore National Laboratory  
P.O. Box 808, L-703  
Livermore, CA 94551

DIRECT TELEPHONE CALLS TO:

Alan H. Thompson  
(925) 422-7820

Customer No.:

The Regents of the University of California  
(type or print identity of assignee of entire interest)

1111 Franklin Street  
(address)

Oakland, CA 94607-5200

☒ Recorded in PTO on 5/18/98  
Reel 9203  
Frame 0235

Date 7/17/00

  
Signature

Janet G. Tulk  
(type or print name of person authorized to  
sign on behalf of assignee)

Laboratory Counsel  
Title

NOTE: The assignee of the entire interest may revoke previous powers and be represented by an attorney of his or her selection. 37 C.F.R. § 1.36.

*(check the following item, if it forms a part of this power of attorney)*

☐ Added page—Authorization of attorney(s) to accept and follow instructions from representative.

(Power of Attorney by Assignee of Entire Interest [12-2]—page 2 of 2)